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NANODISPERSED REFRACTORY COMPOUNDS IN THE ELECTRODEPOSITED METAL COATINGS

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1. Introduction

The electrodeposition technique has a great theoretical and practical significance to obtain composite coatings on metal, metallized ceramic or polymer surfaces. The composite coatings can provide surface properties from both the electrodeposited metal and inorganic compound. The electrodeposition method of composite coating metal - inorganic compounds is used for modifying the surface [1-5].

New dispersed compounds with high electroconductivity, for example, NbTi, NbC_xN_y, PbMo₆S₈, (Pb_{1.2}Mo_{6.4}S₈), TiN/NbN, Cu_{1.8}Mo₆S₈, Sn_{1.2}Mo_{6.4}S₈, YBa₂Cu₃O_{7-x} and Cr₃C_{1.6}N_{0.4} have been prepared by the method of high temperature ion chemical synthesis and the plasma chemical method [5-9].

The aim of our investigations was to determine the possibilities of composite electrodeposition in systems Sn-PbMo₆S₈, Sn-NbC_xN_y, Sn-TiN, Sn-Ti_{0.63}Nb_{0.34}C_{0.38}N_{0.58} and the characteristics of the electrodeposited thin layers' surface structure. These inorganic compounds were chosen to ensure electronic conductivity, solderability and black colour of the coatings.

The complexity of chrome-plating technologies and the necessity of obtaining chromium coatings with different functional properties motivate the search for new types of electrolytes to enable co-deposition of other elements, for example, Cd, Zn, Mo and particles of diamond, B_{6.5}C, B₄C, AlB₁₂, SiC and Al₂O₃ in amount of 0.1-0.5 % for preparation of composite coatings [4, 5].

Our investigations were aimed towards preparation of an electrolyte which allows for the attainment of electrodeposited coatings of Cr-Cr₃C_{1.6}N_{0.4} at temperature 25-30°C.

2. Experimental

The complex electrolyte Sn(IV)-K₄P₂O₇ (Sn - 0.3M, K₄P₂O₇ - 1.7M) was used to electrodeposit composites Sn-Ti_{0.63}Nb_{0.34}C_{0.38}N_{0.58} on copper substrate. The cation active organic compounds were added at 0.6 to 2.5 wt%. To obtain Sn-NbC_xN_y and Sn-Ti_xN_y the complex electrolyte of Sn(II)-K₄P₂O₇ was used with concentrations: Sn-0.3M, K₄P₂O₇-0.8M. Alkylbenzyltrimethylammonium chloride and alkylmethanolbenzylammonium chloride were used as cation active organic compounds. The chemical dissolution of dispersed particles does not occur if the electrolyte pH range is 7.0 - 9.0.

The powders of NbC_xN_y, Ti_xN_y, Ti_{0.63}Nb_{0.34}C_{0.38}N_{0.58}, Cr₃C_{1.6}N_{0.4} were prepared in the Institute of Inorganic Chemistry by plasma chemical synthesis. The characteristic shape of prepared Ti_xN_y, Ti_{0.63}Nb_{0.34}C_{0.38}N_{0.58} is cubic, but particles of Cr₃C_{1.6}N_{0.4} have spherical form (Fig. 1). The average particle size of powders was in the range of 0.01-0.6 μm. The characteristics of the dispersed particles of the inorganic compounds was studied by transmission electron microscopy.

The electrolyte containing (g/l): CrO₃ - 200-250, H₂SO₄ - 2.0-2.5, NH₄F - 4.0 was used as the electrolyte for electrodeposition of Cr-Cr₃C_{1.6}N_{0.4} coatings. Different from the usual electrolytes of the

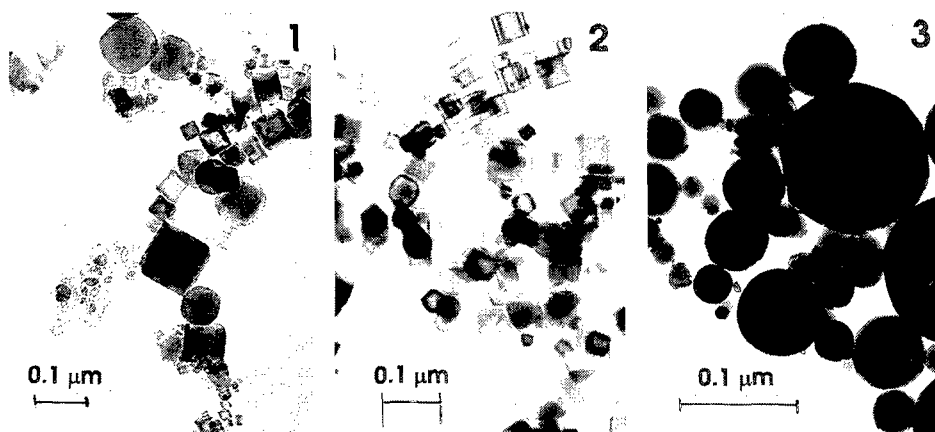


Figure 1. Characteristic shapes and sizes of disperse inorganic compounds: (1) for $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$; (2) for $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$; (3) for $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4}$.

electrodeposition of chromium, our electrolyte contains pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$. The electrodeposition was carried out at temperature of 25-30°C and at cathodic current density $D_c=10-30 \text{ A/dm}^2$.

The charge and velocity of the disperse phase particles were investigated by the microelectrophoresis method. To determine the charge of disperse particles by means of electrophoresis, the horizontally mounted flat cell was used [10]. The content of the disperse inorganic phase in composite coatings was determined by chemical analysis. The quantitative content of chromium carbonitride in composite coatings was determined measuring the amount of carbon by method of combustion in oxygen flow. The surface structure of electrodeposited thin layers was investigated by scanning electron microscopy. We carried out the electrodeposition process in a simple bath of 500 cm^3 volume with mechanical stirring. A cathode and an anode were suspended vertically in the bath.

3. Results and Discussion

3.1. THE COMPOSITE COATING Sn-DISPERSE INORGANIC COMPOUNDS

It has been shown in the microelectrophoresis method, that in a $\text{Sn(IV)}-\text{K}_4\text{P}_2\text{O}_7$ complex $\text{K}_8[\text{Sn}(\text{P}_2\text{O}_7)_3]$ solution and in a $\text{Sn(II)}-\text{K}_4\text{P}_2\text{O}_7$ complex $\text{K}_6[\text{Sn}(\text{P}_2\text{O}_7)_2]$ solution the particles of inorganic compounds NbC_xN_y and $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ possess negative charge, determined by the absorption of complex anions $[\text{Sn}(\text{P}_2\text{O}_7)_3]^{8-}$, $[\text{Sn}(\text{P}_2\text{O}_7)_2]^{6-}$ on the surfaces of particles.

The surface charge of disperse particles does not change in the presence of cation active organic compounds alkylbenzyltrimethylammonium and alkyl-diethanolbenzylammonium chlorides in the electrolyte. Particles maintain their negative charge, but their velocity towards the positively charged electrode decreases. The velocity of the particles is determined by the competition of adsorption processes between complex anions $[\text{Sn}(\text{P}_2\text{O}_7)_3]^{8-}$, $[\text{Sn}(\text{P}_2\text{O}_7)_2]^{6-}$ and cation active organic compounds or the formation of their associates on the surface of disperse particles.

The discharge of tin on the cathode from the complex anion adsorbed on disperse particle in the process of electrodepositing promotes simultaneous particle attachment to the cathode surface and their incorporation in a metal coating. The mechanism of the cathode process in this case determines the possibility of electrodepositing coatings with a high content of disperse particles of inorganic compound in the composite coatings Sn-inorganic compound.

3.2. THE COMPOSITE COATINGS $\text{Sn-Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$

The inorganic compound $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ content in the electrodeposited composite layer does not change significantly with its concentration in the $\text{Sn(IV)-K}_4\text{P}_2\text{O}_7$ electrolyte if pH is 6.5 to 7.0 and a cathodic current density in the range of 3.0 to 17.0 A/dm^2 is used (Fig. 2). The results were obtained from three parallel experiments. The results are relevant to $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ used in this study.

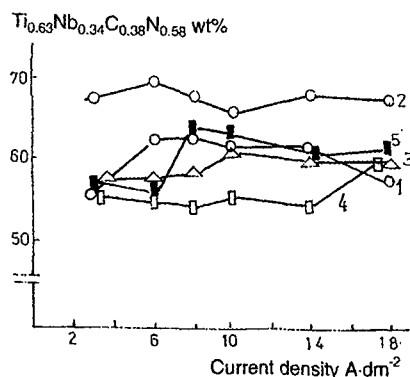


Figure 2. The $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ content in the composite coating $\text{Sn-Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ and its dependence on the concentration of $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ in the electrolyte and the current density D_c :

- (1) $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ 55 g/l, pH 7.0;
- (2) $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ 75 g/l, pH 7.0;
- (3) $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ 75, (I) 4.3 g/l, pH 7.0;
- (4) $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ 75, (I) 4.3 g/l, pH 6.5;
- (5) $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ 100, (I) 4.3 g/l, pH 7.0.

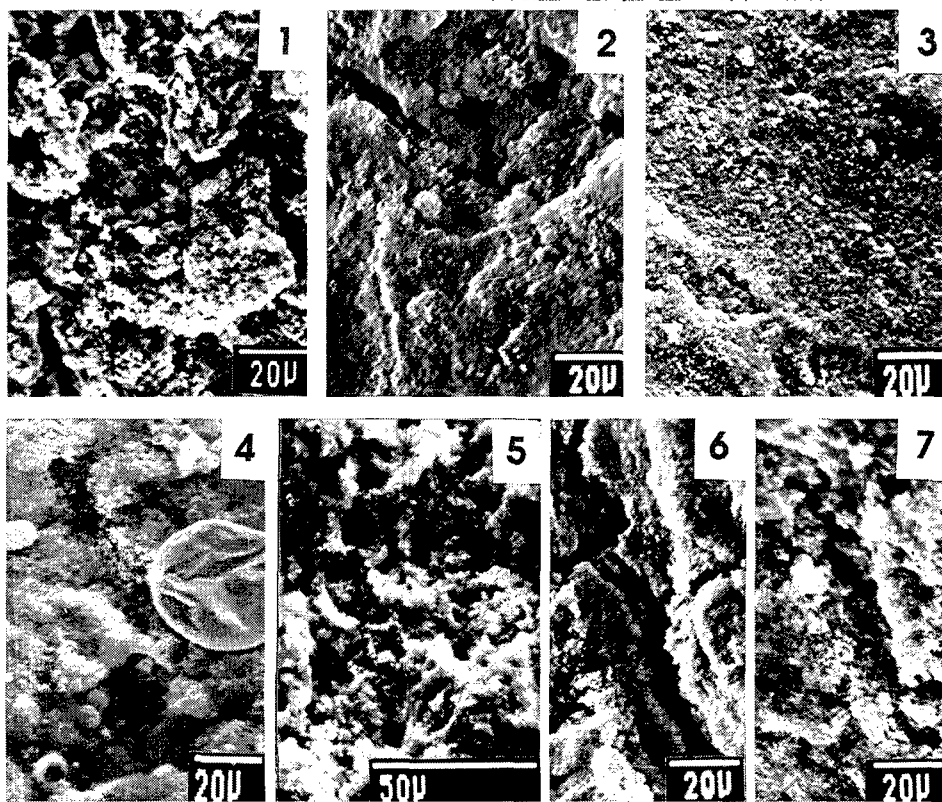


Figure 3. The structure of the composite coating $\text{Sn-Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ and its dependence on the current density (D_c) A/dm^2 : (1) 2.5; (2) 3.5; (3) 6.5, after thermal treatment at 260°C 4 h + 280°C 5 h; (4) 20.0, after thermal treatment at 260°C 4 h; (5) the coating presented at "4" after thermal treatment 280°C 5 h + 310°C 6 h; (6) 24; (7) the coating presented at "6" after thermal treatment 260°C 4 h + 280°C 5 h.

Addition of the cation active compound alkylbenzyltrimethylammonium chloride (I) to the electrolyte does not essentially affect the amount of the disperse phase $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ in the composite layer, but facilitates formation of a homogeneous surface structure without pores and characteristic cracks, if the cathodic current density is $8.0\text{--}10.0\text{ A/dm}^2$ (Fig. 3(2)).

The increase of cathodic current density $>10\text{ A/dm}^2$ is the reason for porous layer formation. The formation of crack-isolated large grains can be observed (Fig. 3(4), (5)). The pore formation is determined by considerable hydrogen evolution on the cathode during electrodeposition of the composite layer. Pores and cracks in the composite layer can be eliminated by 9 hours of thermal treatment at $260, 280, 310^\circ\text{C}$ (Fig. 3(3), (5), (7)). At the beginning of the thermal treatment we can observe the occlusion of organic compound, which is adsorbed on the particles of the disperse phase and cathode surface during the electrodeposition process (Fig. 3(4) A). This could be the reason for the increase in the number of pores, if the thermal treatment is insufficient. The electrodeposited composite layers are electroconductive. The investigations of these layers' properties are continuing.

3.3. THE COMPOSITE COATINGS $\text{Sn-Ti}_x\text{N}_y$

It is possible to electrodeposit composite coatings with disperse phase content of up to 42 - 70 wt% from the $\text{Sn(II)-K}_4\text{P}_2\text{O}_7$ complex electrolyte, where the amount of inorganic compound Ti_xN_y is from 100 to 180 g/l and the concentration of organic substances alkyl-di-(β -hydroxyethyl)benzylammonium chloride mixture with alkyl-di-(β -hydroxyethyl)amin 0.6-2.5 wt%. The dependence of titanium nitride content in a composite coating on the concentration of organic substances in electrolyte and the cathodic current density are demonstrate in Figure 4. The electrodeposited composite layers $\text{Sn-Ti}_x\text{N}_y$ have a characteristic heterogeneous surface structure and cracks in the coating. The coating can easily become homogeneous by thermal treatment at $250\text{--}280^\circ\text{C}$ for 1 h (Fig. 5). Micropores and cracks have been filled after the treatment. The coatings ($10\text{--}20\text{ }\mu\text{m}$) can prevent corrosion and with a content of Ti_xN_y up to 30 wt% have a good solderability.

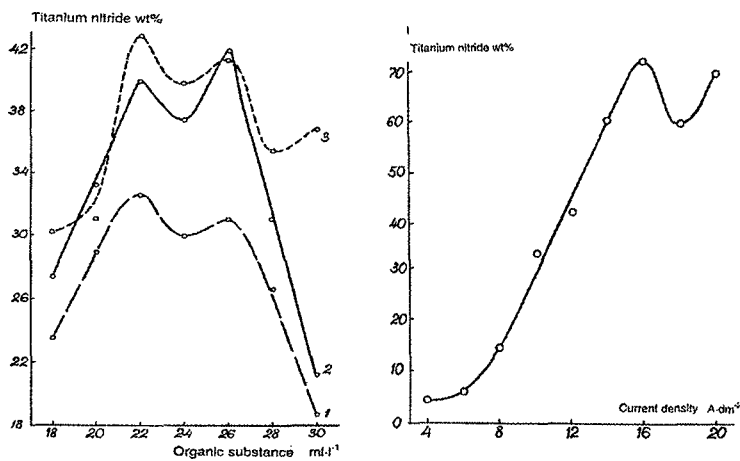


Figure 4. The content of titanium nitride in composite coating $\text{Sn-Ti}_x\text{N}_y$ in dependence on the content of organic substance in electrolyte and the density of cathodic current.

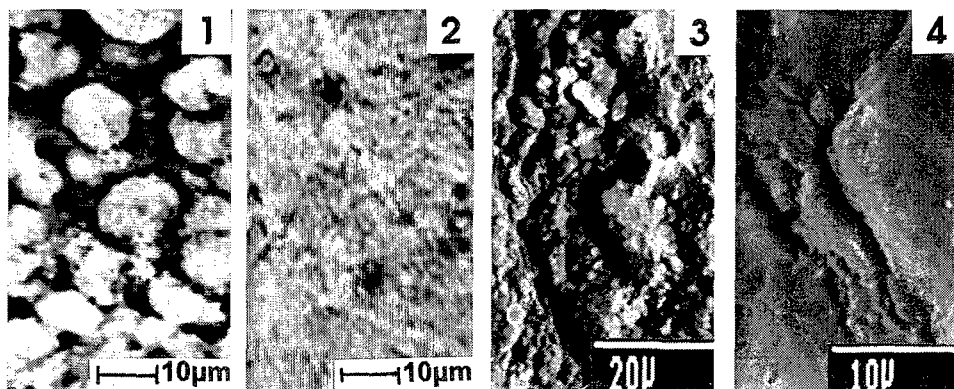


Figure 5. The structures of composite coating in dependence on the content of titanium nitride and thermal treatment: (1) 5.9 wt% without thermal treatment; (2) 5.9 wt% after thermal treatment at 280°C 1 h; (3) 53.6 wt% + 0.5 μm sputtered Sn without thermal treatment; (4) 53.6 wt% + 0.5 μm sputtered Sn after thermal treatment at 250°C 1 h.

3.4. THE COMPOSITE COATINGS $\text{Sn-NbC}_x\text{N}_y$

It is possible to electrodeposit composite coatings with disperse phase contents of up to 85-88 wt% (Fig. 6) from the $\text{Sn(II)-K}_4\text{P}_2\text{O}_7$ complex electrolyte, where the amount of inorganic compound NbC_xN_y is from 100.0 to 180.0 g/l and the concentration of alkylbenzyltrimethylammonium chloride (I) is from 6.4 to 9.0 g/l. Independent of the content of the disperse phase the electrodeposited composite layers $\text{Sn-NbC}_x\text{N}_y$ have a characteristic heterogeneous surface structure and cracks in the coating. The coatings can easily become homogeneous by thermal treatment at 280°C for 4 - 10 hours (Fig. 7). These thin layers are electroconductive and solderable at $300 \pm 10^\circ\text{C}$, if the NbC_xN_y content is < 30 wt%. Homogenized coatings on copper are corrosion resistant, when tested for 30 days at $40 \pm 2^\circ\text{C}$, relative humidity of 98%. They are structure-stable at -50°C .

3.5. THE COMPOSITE COATINGS $\text{Cr-Cr}_3\text{C}_{1.6}\text{N}_{0.4}$

The electrophoretic investigation of chromium carbonitride surface properties depending on ion composition of solution gave the following results. Solutions of polychromium acids in the presence

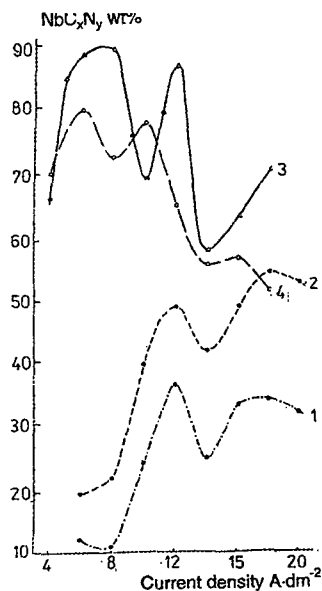


Figure 6. The niobium carbonitride content in the composite coating $\text{Sn-NbC}_x\text{N}_y$ and its dependence on the concentrations of the ultradisperse phase, the organic substance (I) and the current density D_c : (1) NbC_xN_y 100, (I) 6.4; (2) NbC_xN_y 120, (I) 6.4; (3) NbC_xN_y 180, (I) 8.0; (4) NbC_xN_y 180, (I) 9.0 g/l.

of H_2SO_4 and NH_4F or without these additions are strongly acidic and chromium carbonitride particles are positively charged. The chromium carbonitride particles move towards the negative electrode in the electric field with the velocity of 12.1 points/s.

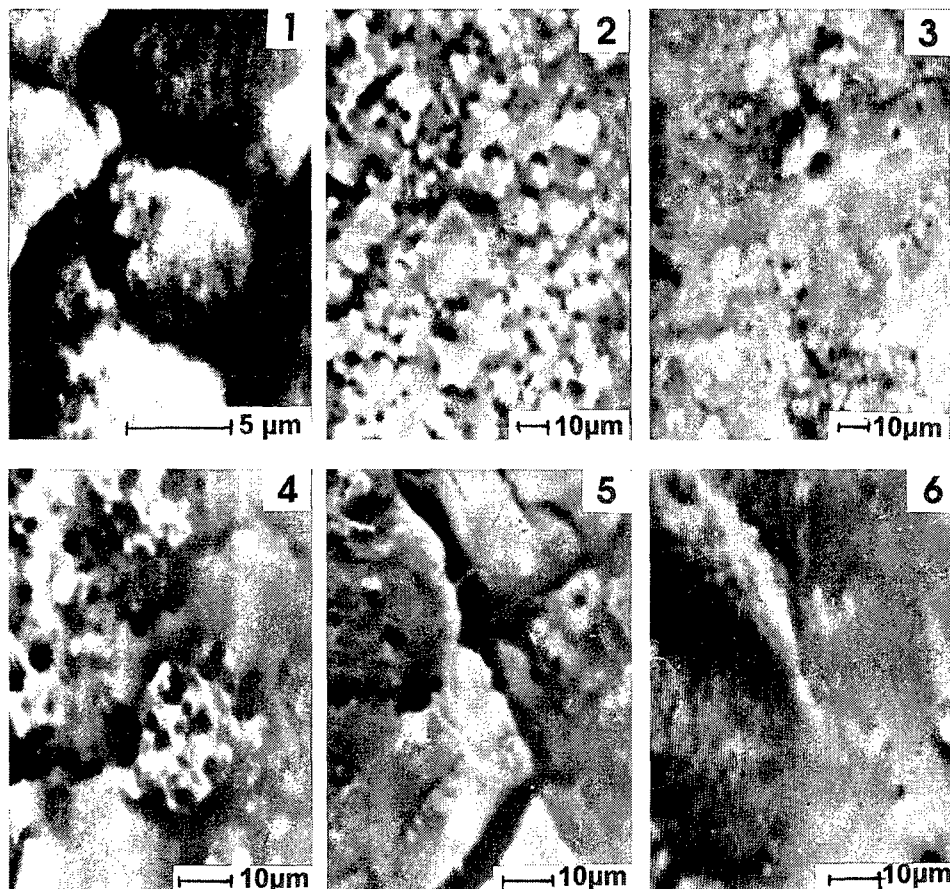


Figure 7. The structure of the composite coating and its dependence on the niobium carbonitride content in the coating $\text{Sn-NbC}_x\text{N}_y$: (1) 9.64 wt% without thermal treatment; (2) 56.96 wt% without thermal treatment; (3) the coating presented at "2" after thermal treatment at 280°C ; (4) 38.4 wt% without thermal treatment; (5) 72.96 wt% without thermal treatment; (6) the coating presented at "5" after thermal treatment at 280°C .

In the presence of pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$, H_2SO_4 being absent, chromium carbonitride particles also have the positive charge, but their velocity decreases to 8.4 points/s. In the electrolyte containing H_2SO_4 (concentration 2.8 g/l) and $\text{H}_4\text{P}_2\text{O}_7$, chromium carbonitride particle motion velocity is determined by the presence of $\text{P}_2\text{O}_7^{4-}$. The co-deposition of chromium carbonitride in the course of electrodeposition of chromium composite coatings as well as during formation of other metal coatings is determined by the complicated mechanism of cathode process and coatings growth [11].

The obtained data reveal that chromium carbonitride percentage in coatings depends on its content in electrolyte, cathodic current density and concentration of $\text{H}_4\text{P}_2\text{O}_7$ (Fig. 8, Fig. 9).

The co-deposition of disperse phase in chromium coating (concentration of disperse phase in electrolyte from 5.0 to 50.0 g/l) is considerably influenced by the cathodic current density. Only when the current density is increased up to 8.0-10.0 A/dm² the formation of homogeneous coatings on the entire surface to be covered begins. At further increase of the cathodic current density up to 20-30 A/dm² the composite coatings are homogeneous in structure without changes on the sharp edges. The highest

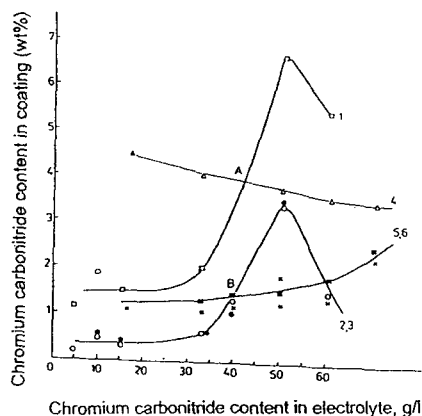


Figure 8. Dependence of chromium carbonitride content in composite coatings on chromium carbonitride and pyrophosphoric acid concentration in electrolyte and cathodic current density:

(1-3) $H_4P_2O_7$ content 3.6 g/l, (1) — 10 A/dm², (2) — 20 A/dm², (3) — 30 A/dm², (4-6) — $H_4P_2O_7$ content 5.4 g/l, (4) — 10 A/dm², (5) — 20 A/dm², (6) — 30 A/dm².

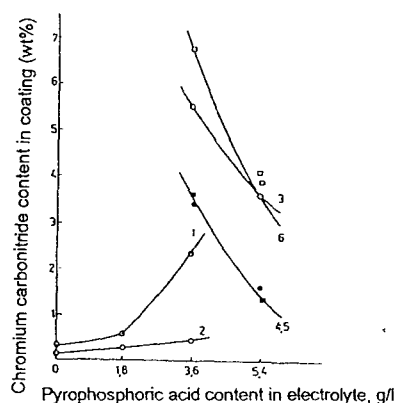


Figure 9. Influence of pyrophosphoric acid concentration in electrolyte on the content of co-deposited chromium carbonitride in composite coatings: (1, 2) concentration of chromium carbonitride 10 g/l, (1) 10 A/dm², (2) 20 A/dm², (3-5) concentration of chromium carbonitride 50 g/l, (3) — 10 A/dm², (4) — 20 A/dm², (5) — 30 A/dm², (6) — concentration of chromium carbonitride 60 g/l, $D_c=20$ A/dm².

possible degree of co-deposition of chromium carbonitride (up to 6.6 wt%) occurs at its concentration in solution of 50.0 g/l and cathodic current density of 10.0 A/dm². When the content of chromium carbonitride in electrolyte is 40.0 g/l and concentrations of $H_4P_2O_7$ are 3.6 and 5.4 g/l the content of disperse phase in coatings is mainly determined by cathodic current density.

The structures of electrodeposited coatings give additional information on mechanism of composite coating formation and purposefulness of the choice of concentration of disperse phase of inorganic compound and additional anion in electrolyte (Fig. 10). The structure (2) is determined by rivaling processes of electrodeposition of glittering chromium coatings versus the formation of chromium-chromium carbonitride composition with co-deposition of disperse phase in amounts of 0.2 wt%. The increase of chromium carbonitride concentration in electrolyte up to 50.0 g/l (the content of $H_4P_2O_7$ being 5.4 g/l and cathodic current density 20.0 A/dm²) ensures the co-deposition of chromium carbonitride up to 3.5 wt% (structures (7) and (8)). In this case the increase of $H_4P_2O_7$ concentration up to 12.0 g/l changes the character of structure and ensures its homogeneity and compactness (structure (9)). When the chromium carbonitride and pyrophosphoric acid concentrations are simultaneously increased up to 95.0 g/l and 15.0 g/l respectively at cathodic current density of 26.0 A/dm² the structure is homogeneous with round, sheet-shape crystal grains over all the surface, compact, without pores (Fig. 10, structures (11) and (12)).

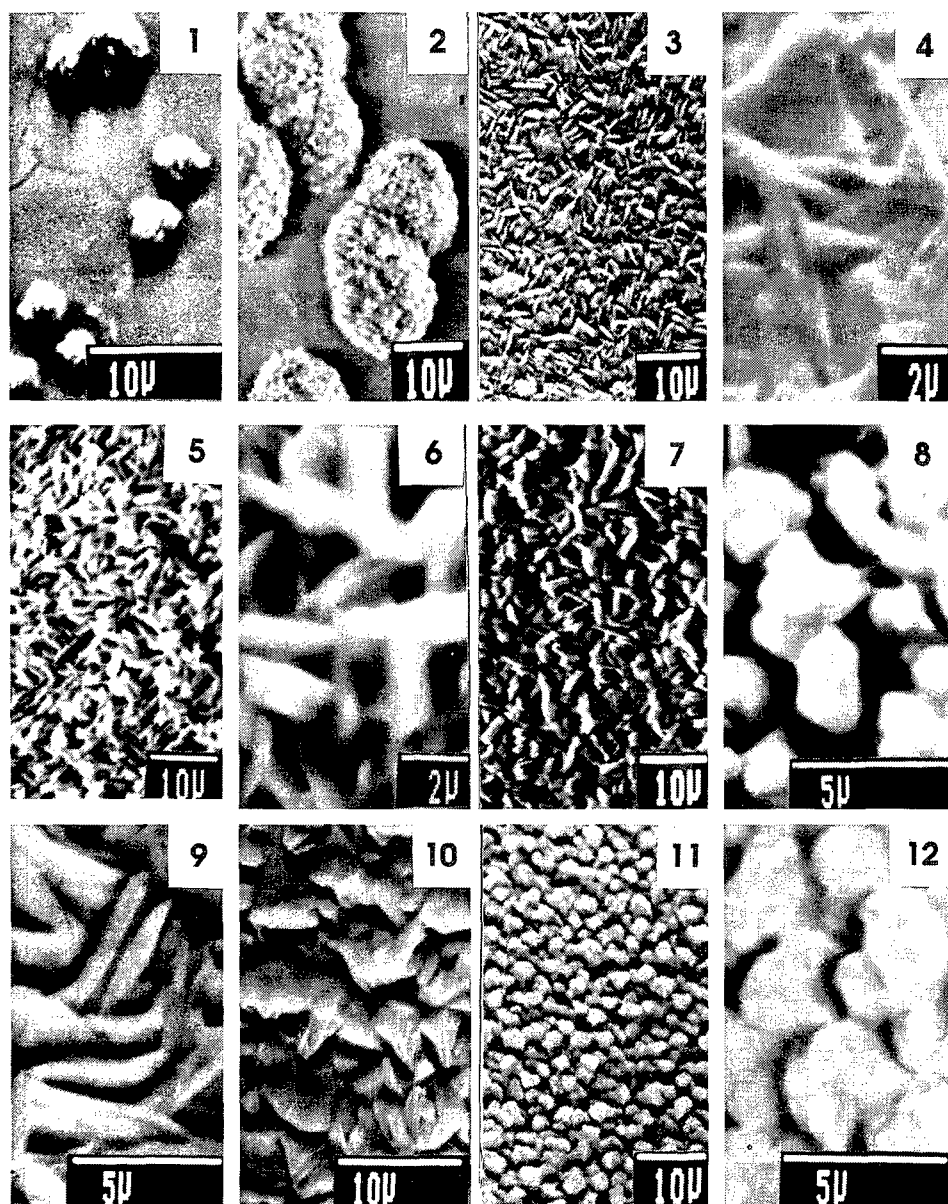


Figure 10. Changes of the surface structure of chromium-chromium carbonitride composite coating depending on chromium carbonitride $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4}$ and pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$ content in electrolyte (g/l) and cathodic current density (D_c): (1) the electrolyte not containing $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4}$ and $\text{H}_4\text{P}_2\text{O}_7$ at $D_c=3.5 \text{ A/dm}^2$; (2) content $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4} - 6.0$ without $\text{H}_4\text{P}_2\text{O}_7$ at $D_c=10 \text{ A/dm}^2$; (3, 4) $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4} - 6.0$, $\text{H}_4\text{P}_2\text{O}_7 - 1.8$, $D_c=10 \text{ A/dm}^2$; (5, 6) $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4} - 7.4$, $\text{H}_4\text{P}_2\text{O}_7 - 10.0$, $D_c=26 \text{ A/dm}^2$; (7, 8) $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4} - 50.0$, $\text{H}_4\text{P}_2\text{O}_7 - 3.6$, $D_c=20 \text{ A/dm}^2$; (9) $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4} - 50.0$, $\text{H}_4\text{P}_2\text{O}_7 - 12.6$, $D_c=20 \text{ A/dm}^2$; (10) $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4} - 39.0$, $\text{H}_4\text{P}_2\text{O}_7 - 0.0$, $D_c=15-20 \text{ A/dm}^2$; (11, 12) $\text{Cr}_3\text{C}_{1.6}\text{N}_{0.4} - 96.0$, $\text{H}_4\text{P}_2\text{O}_7 - 12.6$, $D_c=26 \text{ A/dm}^2$.

4. Conclusions

1. It is possible to obtain the following nanocomposite surface coatings by electrodeposition on copper as the base metal:

- $\text{Sn-Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ with the $\text{Ti}_{0.63}\text{Nb}_{0.34}\text{C}_{0.38}\text{N}_{0.58}$ content from ~55 to 70 wt% from the $\text{Sn(IV)-K}_4\text{P}_2\text{O}_7$ electrolyte;
- $\text{Sn-NbC}_x\text{N}_y$ with the NbC_xN_y content from ~10 to 88 wt% from the $\text{Sn(II)-K}_4\text{P}_2\text{O}_7$ electrolyte;
- $\text{Sn-Ti}_x\text{N}_y$ with the Ti_xN_y content from ~42 to 70 wt% from the $\text{Sn(II)-K}_4\text{P}_2\text{O}_7$ electrolyte.

2. The formation of the electrodeposited composite layers' surface structure is determined by the applied cathode current density, hydrogen evolution in the electrolysis process and the amount of the disperse phase in the composite.

3. Pores and cracks in the composite layers can be eliminated by 4-40 h thermal treatment at 260-310°C.

4. The electrolyte based on CrO_3 in the presence of H_2SO_4 and NH_4F at temperature of 20 to 30°C and cathodic current density of 10 to 30 A/dm^2 result in deposition of the chromium-chromium carbonitride composite coatings. The disperse phase content varies from 0.2 to 6.8 wt% depending on the content of chromium carbonitride and additional anion $\text{P}_2\text{O}_7^{4-}$ in electrolyte.

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